

## Analysis of the Effect of Pollution of Component Surfaces as a Result of Possible Contact of Fresh Nuclear Fuel with Sea Atmosphere on Corrosion

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Received: July 20, 2022. Revised: May 22, 2023. Accepted: June 05, 2023.

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### Abstract

Acquisition and 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 is 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.

**Keywords:** reactor; clad zirconium alloy E-110; corrosion; sea atmosphere; standard coolant; coolant pollution.

### 1. 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<sub>2</sub> (6 g/L), KCl and CaCl<sub>2</sub> (1 g/L each) [1]–[8]. 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 [7], [9].

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 [7].

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 [7].

Thus, the conditions appear for electrochemical processes on metal surfaces. As indicated in the paper of [1], [7], 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 fuel assemblies (FAs) 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.

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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 [7].

Alongside with the above-said, one should take into account that the ocean water contains iodine. This element is hazardous for zirconium and under definite conditions could cause its cracking. Therefore, it was interesting to evaluate the effect of the increase in content of iodine in the coolant on corrosion of alloy E-110.

## 2. Goal of research

Justification of safety of storage of fresh FAs in sea atmosphere and assessment of the effect of possible pollution of assembly components with substances, contained in such atmosphere, on corrosion of structural materials of FAs in their further operation.

## 3. 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 [3] focuses on the effect of concentration of  $\text{Cl}^-$  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 Fig. 1. The curve of alloy corrosion in water without addition of chlorides is also presented there [7].

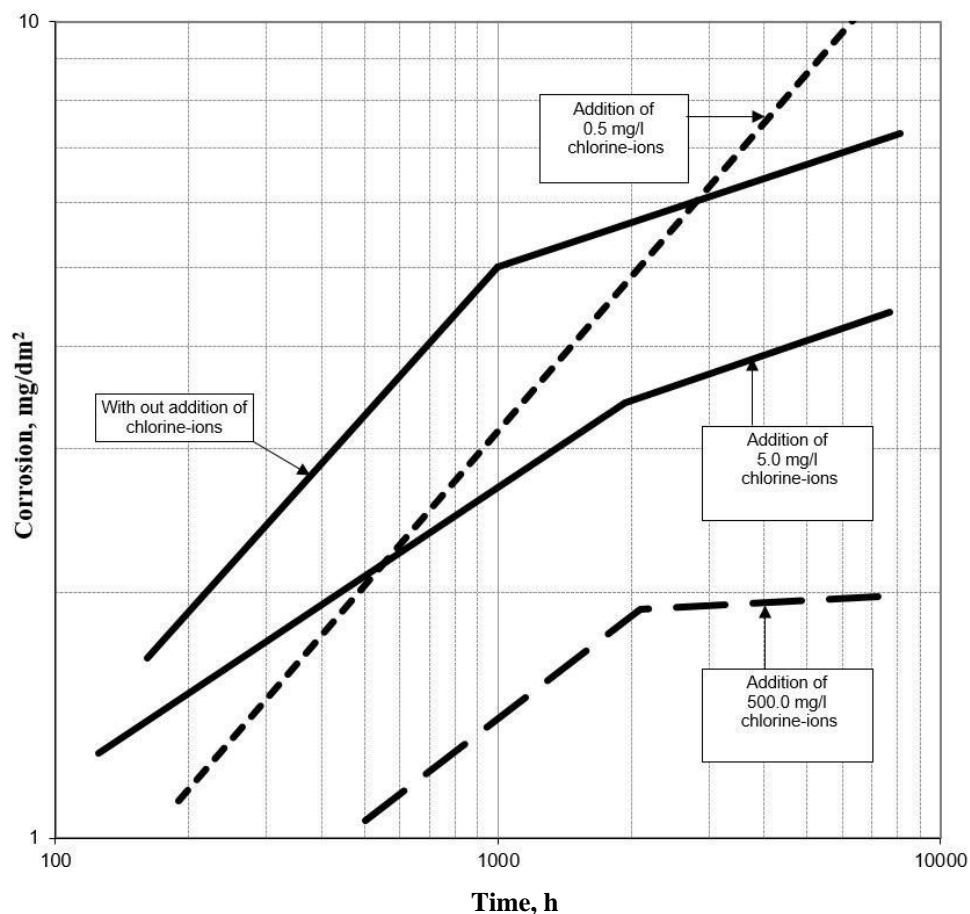


Fig. 1. Corrosion of alloy E-110 at 300 °C in water with different content of chlorides.

We can see 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 [7].

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 Fig. 2, and the noticeable braking in discharging process of depolarizer ions. The higher the braking of cathodic discharge process of depolarizer ions is, that is, the higher the slope of a curve in Fig. 2, the greater is the rate of corrosion decrease of zirconium alloy E-110 [7, 8].

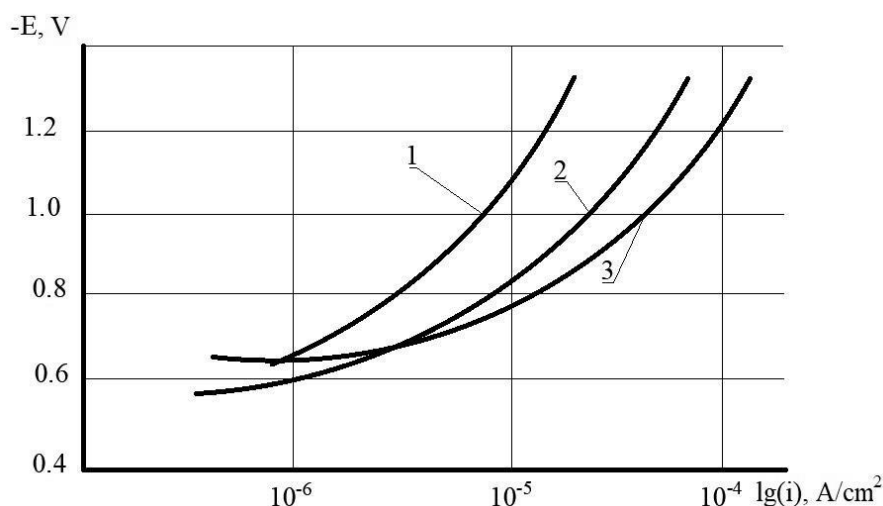


Fig. 2. Cathodic polarization curves of alloy Zr – 1 % Nb at 300 °C in distilled water containing different amount of chlorine-ions: 1 – 500 mg/L  $\text{Cl}^-$ ; 2 – 5 mg/L  $\text{Cl}^-$ ; 3 – 0.5 mg/L  $\text{Cl}^-$ .

Summarizing the above-mentioned, on the basis of the paper of [3], 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.

#### 4. 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  $\text{I}_2$  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 (Fig. 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 [7].

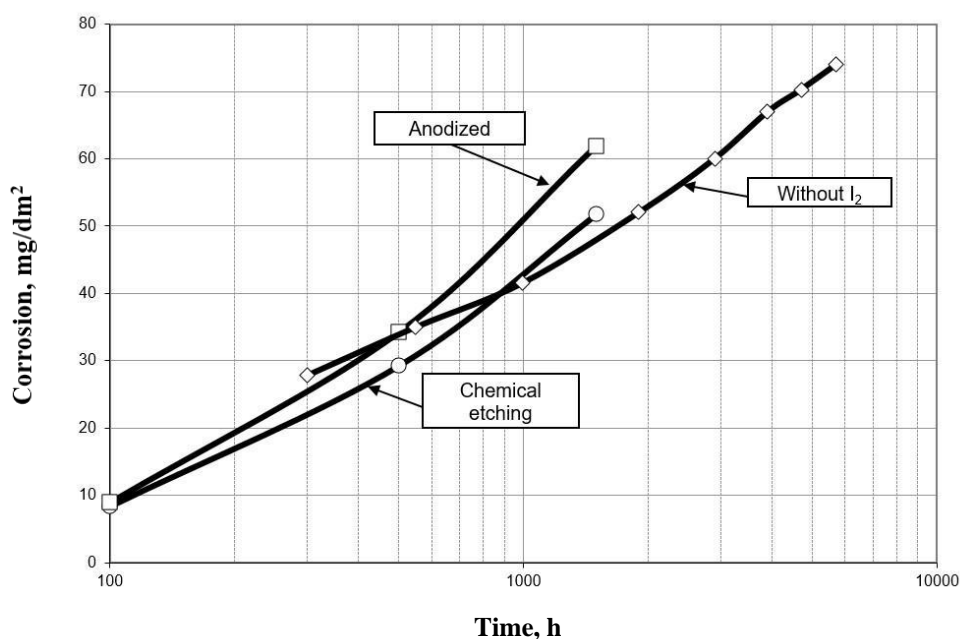
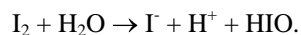


Fig. 3. Corrosion of alloy E-110 at 350 °C and 12 MPa in non-deaerated water with addition of 2.5 mg/kg I<sub>2</sub>.

According to reference data of [6], 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 [3] consider that ions of iodine and bromine (content of bromine in ocean water according to the data of [7] 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:



Oxy acids are strong oxidizers and displace the shift in the stationary potential to the region of positive potentials. The paper of [3], [7] describes the experiments when the specimens of zirconium alloys, loaded with bending or axial tension, were polarized with current of 1.6 mA/cm<sup>2</sup>. 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 [7], [8]. The pits and cracks were filled with corrosion products of black colour. The authors of paper of [3], [7] 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:



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<sup>-</sup>, Br<sup>-</sup> or I<sup>-</sup>) 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 [7], [10]–[12].

## 5. Conclusion

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

Fuel handling procedures shall not be used, unless there is an urgent need, to reduce a possibility of loss of the packing integrity. When loading the fresh FAs into the reactor core, the daily monitoring of content of chlorine-ion in the coolant shall be performed. Bringing the reactor to nominal power shall be performed only at reaching the standard indices of water chemistry as to chlorides.

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## Аналіз впливу забруднень поверхні деталей у результаті можливого контакту свіжого ядерного палива з морською атмосферою на корозію

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## Анотація

Виконано збирання та аналізування інформації щодо можливого впливу компонентів морської атмосфери у разі забруднення ними поверхні збірок на корозію конструкційних матеріалів деталей тепло-видільних збірок водо-водяного енергетичного реактора ВВЕР-1000 за їх подальшої експлуатації. Наведено дані статичних і динамічних випробувань сплаву Е-110 за температур 300–350 °С у воді та у штатному теплоносії реакторів, забруднених хлоридами і йодом, а також сплаву Е-110 за спеціального забруднення його поверхні хлоридами. Показано, що у разі дотримання умов зберігання свіжого палива, а також рекомендацій цієї роботи забезпечується його висока корозійна стійкість і працездатність під час подальшої експлуатації.

**Ключові слова:** реактор; оболонковий цирконієвий сплав Е-110; корозія; морська атмосфера; стандартна охолоджувальна рідина; забруднення теплоносія.