https://doi.org/10.46813/2024-153-095

ANALYSIS OF THE INNER SURFACE OF A SUPERCRITICAL WATER CONVECTION LOOP AFTER AN ELECTRON IRRADIATION SESSION

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Supercritical water (SCW) can be an effective cooler for nuclear reactors. All sorts of research on the subject of SCW are very important, especially bearing in mind that SCW is a non-polar solvent, while subcritical water is a polar solvent. Irradiation leads to an increase in corrosion and migration of some metals into the volume of the SCW. The transition from the supercritical state to the normal state and inversely contributes to the synthesis of substances in the SCW. On the inner surface of the convection loop, a film of corrosion products is formed, which are minerals that can protect the metal from corrosion.

PACS: 82.80.-d; 07.35.+k; 29.20.Ej

INTRODUCTION

To conduct experiments on the study of corrosion in supercritical water, a device was manufactured in the form of a rectangular loop 1.5x1.2 m with rounded corners and a welded irradiation chamber and a total volume of approximately 3.9 liters. The supercritical water convection loop was made of a steel pipe (12X18H10T) with a thickness of 4 mm and an inner diameter of 32 mm. It is known that SCW can be an effective cooler for nuclear reactors, but the high temperature and pressure require stable materials to build the equipment. It is generally accepted that supercritical aqueous convection loops are used to study the corrosion of structural materials under the influence of radiation and coolant flow [1, 2]. The effect of radiation only increases corrosion and significantly reduces the strength characteristics [3]. We have conducted some studies on the behavior of stainless steel in the SCW [4, 5]. It was found that the water circulating in the loop is enriched with metal ions in accordance with the composition of the structural steel. On the inner surface of the loop, a plaque (osuga) is formed, consisting of metal compounds. This plaque has some protective properties.

1. CONDITIONS FOR CONDUCTING EXPERIMENTS ON LOOPS

The loop body, made of austenitic steel, passed a successful 1600 h test in a total of three sessions (2012, 2019, and 2021) in a convection water flow environment in a subcritical and supercritical state. Thermal processes occurring in the irradiation chamber (IC) have been investigated in [1, 2]. At the lower entrance to the IC, the control system maintained the characteristic circulation temperature of the coolant Tin = 360 °C, obviously less than the critical water temperature Tc = 374 °C. It was measured by a set of thermocouples located outside the irradiation zone (direct thermometry is difficult inside it). Calculations show an increase in the average cross-sectional temperature to 368 °C before leaving the IC and subsequent cooling. The temperature of the output thermocouple was 364 °C for channels II and III IC and 350 °C for tubes I and IV on the outer surface [6]. Measurements by remote optical pyrometry under electron irradiation showed a temperature of 400...420 °C. In [1], it was shown that the interiors of massive ICs can also be about 10... 15 °C is hotter than the predicted reference coolant temperature. Thus, the supercritical transition occurs directly within the IC near the irradiated samples. The water pressure in the loop was maintained at 23.5 MPa. The electron beam at the output of the LPE-10 accelerator during the IC irradiation session had an average energy of 10 MeV and an average electron beam current of 0.71 mA. The pulse frequency of the electron beam was 250 Hz. The pulse duration is 3.5 μs. The scanning frequency of the beam through the irradiation chamber is 3.7 Hz. The average vertical span of the beam in the plane of the irradiation chamber is 19 cm. The maximum fluence on the surface of the irradiation chamber reached $2 \cdot 10^{20}$ el/cm^2. In 2021, during a 575 h experiment to irradiate metal samples for corrosion tests, water was fed to the bottom of the loop at an average rate of 1.5 ml/min. Fig. 1 shows the places where photos of the inner surface of the loop were taken (Figs. 2–5).

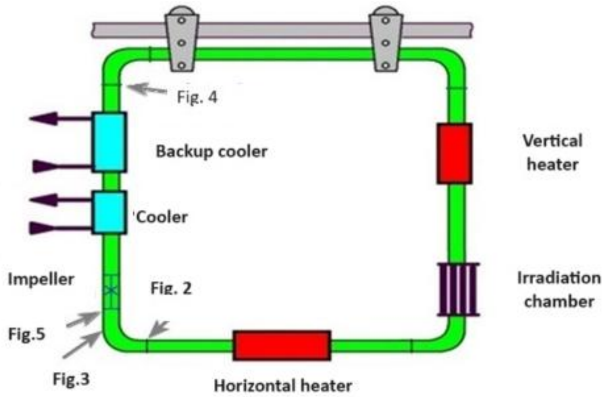

Fig. 1. Supercritical Water Convection Loop

The entire inner surface of the loop is covered with a light coating, which is unevenly distributed. In Fig. 3, there are more deposits on the inner walls of the loop than in Figs. 2, 4, 5.

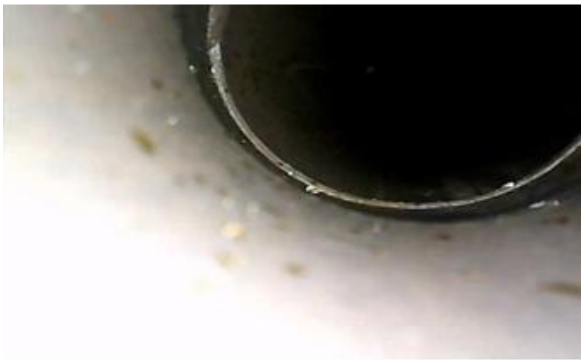

Fig. 2. Photo of the pipe seam after the horizontal heater

Fig. 3. Photo of the inner surface of the pipe below the impeller at the turn

2. CHARACTERISTICS OF MAKE-UP AND CIRCULATING WATER

The composition of the water that was fed into the loop is presented in Table 1. From the top of the loop, circulating water was taken for research at the same rate as it was supplied, i.e. 1.5 ml/min. To conduct a selective chemical analysis of water on the ICPE-9000 Shimazu spectrometer, 25 samples with a volume of

Fig. 4. Photo of the seam of the pipe above the coolers

Fig. 5. Photo of the impeller below

50 ml were collected daily from the loop. The results of their analysis are shown in Table 2.

As can be seen from the data in Table 2, there is a slight decrease in the concentration of metal ions in the water during the research session. This is especially evident for chromium and nickel. This may indicate a decrease in corrosion, due to which metal ions enter the water. Almost all water samples from the loop contain chromium, which was practically absent in the original water, which also indicates corrosion of stainless steel.

Table 1

Composition of water samples at the inlet to the loop, mg/l

No	Fe	Mn	Ni	Cr	Ca	Cu	Mg
1	–	0.004	–	0.0148	0.0122	0.117	0.126
2	–	–	–	0.0091	–	–	–
3	–	–	–	0.001	–	–	–

Table 2

Composition of water samples at the outlet of the loop, mg/l

No	Fe	Mn	Ni	Cr	Ca	Cu	Mg
1	–	0.007	0.024	0.677	2.770	0.020	0.198
2	0.001	0.005	0.015	0.617	1.690	0.026	0.137
3	–	0.003	0.007	0.440	0.939	0.029	0.093
4	–	0.002	0.004	0.116	0.357	0.022	0.053
5	–	0.001	0.002	0.021	0.119	0.015	0.029
6	–	–	–	0.004	–	0.004	–
7	-	–	–	0.005	–	0.003	–
8	–	–	–	0.003	–	–	–
9	–	–	–	0.010	–	0.678	–
10	–	–	–	0.001	–	0.002	–
11	–	–	–	0.001	–	–	–

12	–	–	–	0.062	–	–	–
13	–	–	–	0.025	–	–	–
14	–	–	–	0.018	–	–	–
15	–	–	–	0.009	–	–	–
16	–	–	–	0.006	–	–	–
17	–	–	–	0.016	–	–	–
18	–	–	–	0.054	–	–	–
19	–	–	–	0.094	–	–	–
20	–	–	–	0.030	–	–	–
21	–	–	–	–	–	–	–
22	–	–	–	–	–	–	–
23	–	–	–	–	–	–	–
24	–	–	–	–	–	–	–
25	–	–	–	–	–	–	–
Limit of detection μg/l	0.1	0.03	0.3	0.3	0.005	0.4	0.005

Notes: '– ' means that the content of these elements is below the detection limit of the ICPE-9000 spectrometer. The limit of detection is calculated for a solution of one element and changes according to the matrix.

3. PROBABLE CAUSES OF CORROSION REDUCTION

In accordance with the hydrothermal method of obtaining inorganic compounds [7], which is based on the properties of water at high temperatures and pressures, when insoluble under normal conditions, such as oxides, phosphates, and others, insoluble under normal conditions, the synthesis of new substances can take place in aqueous solutions. With a cyclical change in water parameters in the loop, that is, a decrease in temperature and the transition of water to a normal state, and then again to the SCW, the dissolution and precipitation of inorganic substances occurs almost simultaneously, and the processes of formation of new substances are accelerated. It should also be borne in mind that SCW is similar in properties to organic solvents and it rejects inorganic substances from its environment. For our composition of water, such compounds as spinels can be formed – cuprospinel ($(Cu,Mg)Fe_2^{+3}O_4$); magnetite ($Fe^{+2}Fe_2^{+3}O_4$); magnesioferrite ($MgFe_2^{+3}O_4$); magnesiochromite ($MgCr_2O_4$); nichromite ($NiCr_2O_4$); trevorite ($NiFe_2^{+3}O_4$): chromatite ($CaCr_2O_4$); chromite. Since steel contains titanium, formation of ulvospinel ($TiFe_2^{+2}O_4$) is possible [8]. In addition to these spinels, there may be phosphates (up to 0.019% phosphorus in steel) of the following composition: phosphoferrite ($(Fe,Mn)_3(PO_4)_2 \cdot 3H_2O$); phosphosiderite ($FePO_4 \cdot 2H_2O$) red-coloured; vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$) blue-colorued. All these substances are weakly soluble minerals and their layer on the steel surface can inhibit corrosion.

CONCLUSIONS

A decrease in the concentration of heavy metal ions in the circulating water may be due to a decrease in corrosion due to a layer of sediments on the inner surface of the loop. The sediments probably include a variety of spinels and phosphates. In Figs. 2, 4, 5, even on the weld, we see few traces of corrosion. Fig. 3 shows traces of corrosion in a larger size, in this area we have a turbulent flow of SCW, which contributes to mass transfer and, as a result, increases corrosion. Despite the fact that the inflow of metal ions into the SCW was indicated, no traces of significant corrosion were found. The loop has withstood almost 1600 h of operation in the SCW environment and is capable of operating in the future. These are preliminary results, further research will be continued

ACKNOWLEDGEMENTS

This work was carried out at the expense of the budget program "Support for the Development of Priority Areas of Scientific Research" (КПКВК 6541230).

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Article received 25.09.2024

АНАЛІЗ ВНУТРІШНЬОЇ ПОВЕРХНІ НАДКРИТИЧНОЇ ВОДНОЇ КОНВЕКЦІЙНОЇ ПЕТЛІ ПІСЛЯ СЕАНСУ ОПРОМІНЕННЯ ЕЛЕКТРОНАМИ

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Надкритична вода (НКВ) може бути ефективним охолоджувачем ядерних реакторів. Всілякі дослідження на тему НКВ дуже важливі, особливо маючи на увазі, що НКВ є неполярним розчинником, тоді як докритична вода – це полярний розчинник. Опромінення призводить до зростання корозії і міграції деяких металів у об’єм НКВ. Перехід з надкритичного стану в звичайний і обернено сприяє синтезу речовин у НКВ. На внутрішній поверхні конвекційної петлі утворюється плівка з продуктів корозії, які являють собою мінерали, що здатні захищати метал від корозії.