Reduction of radioactive contamination of surface of steel structures of contour NPP equipment

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Abstract. Reduction in the rate of corrosion of constructional materials leads to increase in level of ensuring radiation safety at operation of NPS. It is possible to improve a radiation situation also due to decrease in sorption of radionuclides on the internal surfaces of the equipment. In this regard authors considered possible ways of decrease in sorption of radionuclides $^{60}$Co and $^{137}$Cs by a surface perlity and alloyed their radioactivity, steely for the purpose of decrease. Results of experiments on sorption of radionuclides are presented and her communication with the size of equilibrium electrochemical potential is noticed. It is shown that sorption of Cs-137 honor 10 times more sorption Co-60. At transfer of steel to a passive state by passivation in nitric acid ($\text{pH} = 3$) considerable decrease in sorption of radionuclides $^{60}$Co, $^{137}$Cs (at 7-10 times) in comparison with not passivated steel is observed. Processing as alloyed, and perlity steel of a zolyama of oxide of aluminum allows to reduce sorption of radionuclides in addition. Additive of colloidal solution - zoli $\text{Al}_2\text{O}_3$ in the passivating sour azotonitratny solutions allows to increase considerably protective properties of the formed coverings and to prevent development of local types of corrosion (ulcers, pittings, cracking).

1. Introduction
One of the main problems arising during the operation of nuclear power plants is the presence of high gamma-radiation background in the reactor equipment. As a result, staff access to such equipment is severely limited. Ensuring radiation and technical safety at NPP facilities is achieved by implementing an integrated approach to solving this complex problem during the operation of nuclear power plants (NPI) [1-4]. During operation, radioactive corrosion products accumulate on the internal surfaces of the NPP contour equipment, and during long-term reactor operation, the activity of the $^{60}$Co radionuclides (mostly long-lived $^{60}$Co) is at least 90% of the total sediment activity. The main source of radioactive cobalt are corrosion products of stainless steel containing 10% nickel, in which there is a lot of cobalt impurities [5-8]. And the higher the corrosion resistance of structural steels (which can be achieved through passivating treatments), the smaller the amount of corrosion products transferred into the coolant, and the less they will be activated in the neutral field of a nuclear reactor [9-11].

2. Relevance, scientific significance of the issue
The chemical methods used for decontamination of the contour equipment of nuclear power plants in addition to technological difficulties lead to the formation of significant amounts of liquid radioactive waste based on spent decontamination solutions [12-15]. The most effective method of improving the radiation situation is to reduce the sorption of radionuclides on the internal surfaces of equipment.
Reducing the corrosion rate of structural materials leads to an increase in the level of radiation safety in the operation of nuclear power plants (NPI) by reducing the activation of structures and reducing the amount of radioactive waste, which determines the relevance of this research direction [16-21].

In this regard, the authors considered possible ways to reduce the sorption of radionuclides $^{60}$Co and $^{137}$Cs by the surface of pearlite and alloyed steels in order to reduce their radioactivity. From a scientific point of view, it is necessary to establish the effect of reducing the sorption of radionuclides by the surface of steel structures due to their treatment with passivating solutions.

When studying sorption of radionuclides of radionuclides $^{60}$Co and $^{137}$Cs samples became (carbonaceous pearlitny steel of the St20 brand and chromonickel austenov brand 08X18H10T steel), representing is longitudinal the tubes of the steam generator 50 mm long sawn in half with the surface area of $50\text{ cm}^2$, placed in glass glasses with the water environment containing the specified radionuclides. The specific activity of the water environment was $(2-5) \times 10^6 \text{ Bq/l}$. The endurance of samples was carried out at $20-25 \degree \text{С}$ and at periodic hashing during the time sufficient for achievement of sorption balance. The ratio the volume of solution/surface area of samples was supported by equal $10/1 \text{ cm}^3/\text{cm}^2$. On reaching sorption balance samples were taken from the water environment, washed out the distilled water, dried up on air.

Measurement of activity was taken on a scintillation gamma and beta spectrometer of "Progress-BG(P))" with use of gamma paths of a spectrometer of SKS-99 "Sputnik".

3. Results and discussion

Results of experiments on sorption of radionuclides the surface of steel have shown that sorption of caesium-137 honor 10 times more cobalt-60 sorption. At the same time communication of sorption with the size of the equilibrium electrochemical potential (REHP) is noted - the REHP is higher, the sorption is lower. The greatest she on the steel processed by hydrochloric acid where stationary potential minimum, and the smallest – on the samples processed by aluminum nitrate solution with nitric acid where electrochemical potential greatest (Figure 1).

It is obvious that what has more positively loaded the surface of metal, pushing away from it positive ions comes that more and, as a result, sorption decreases. More positive ions of $\text{Co}^{2+}$ make a start from a positively charged surface more than ions $\text{Cs}^+$ [4-5]. On the surface of perlitny steel which in these conditions is in an active state the return picture is observed – sorption $^{60}$Co considerably surpasses sorption $^{137}$Cs.

Both perlitny ST-3 steel, and the alloyed steel 08X18H10T subjected to processing zoly Al$_2$O$_3$ at 7-10 times reduces sorption of radionuclides of $^{60}$Co and $^{137}$Cs (Figure 2).

Processing as alloyed, and perlitny steel of a zolyama of oxide of aluminum allows to reduce sorption of radionuclides in addition: a) on $^{137}$Cs on the alloyed steel by 6 times, and on perlitny steel - by 9 times; b) on $^{60}$Co on the alloyed steel by 6 times, and on perlitny steel - by 4 times.

Additive of colloidal solution - zola Al$_2$O$_3$ in the passivating sour azononitratny solutions allows to increase considerably protective properties of the formed coverings and to prevent development of local types of corrosion (ulcers, pittings, cracking, etc.). Ions of aluminum are necessary for initiation of formation of sheetings on those sites of a surface of metal where there are no centers of crystallization of oxides, i.e. on active sites.
Figure 1. Kinetics sorption of radionuclides $^{137}$Cs and $^{60}$Co on the surface of steel after passivation in nitric acid (50mg/l, pH =3): 1 - the alloyed steel 08X18H10T; 2 - perlitovy steel St20

Figure 2. Kinetics sorption of radionuclides $^{137}$Cs and $^{60}$Co on the surface of steel after passivation in nitric acid (50mg/l, pH =3) + a hydrosol of Al$_2$O$_3$ (V) (10mg/l) + processing by sodium nitrite (10mg/l): 1 - the alloyed steel 08X18H10T; 2 - perlitovy steel St20
When considering the issues of decontamination, a well-known method of cyclic treatment of redox solutions using hydrogen peroxide and hydrazine as chemical reagents was taken as the basis [22]. At the same time, the addition of trace amounts of sulfate ions (5-10 mg/kg) to the hydrogen peroxide solution greatly increased the efficiency of the oxidizing solution. This circumstance combined with the use of new components of the redox solution makes the technology of cyclic deactivation easier and more efficient.

Since the decontamination process can be combined with reactor cooling down, it is advisable to start the treatment with a reducing solution that works at a higher temperature than the oxidizing one, i.e. upon reaching 130-140 °C, hydrazine hydrate should be introduced into the circuit at the rate of 30 mg/kg. The treatment with the reducing solution is carried out at a temperature of 100-130 °C for 4 hours or more. Then the temperature is lowered to 60 °C and hydrogen peroxide and potassium sulfate are introduced into the circuit. Processing with an oxidizing solution is carried out for 3-4 hours at maximum flow rates, alternating this process with periodic shutdown and switching of the main circulation pump. Cleaning the coolant on mechanical and ion-exchange filters should be done at the end of the circuit processing with an oxidizing solution, since hydrazine and sulfates are trapped by ion-exchange filters.

The number of processing cycles carried out with redox solutions primarily depends on the time available at the station’s personnel for decontamination. 2-3 cycles are optimal. If the time allotted for decontamination does not exceed 1 day, then processing with only one oxidizing solution is possible.

4. Conclusion

Results of experiments on sorption of radionuclides are presented and her communication with the size of equilibrium electrochemical potential is noticed. It is shown that sorption of $^{137}$Cs honor 10 times more sorption $^{60}$Co. At transfer of steel to a passive state by passivation in nitric acid (pH =3) considerable decrease in sorption of radionuclides $^{60}$Co, $^{137}$Cs (at 7-10 times) in comparison with not passivated steel is observed. Processing as alloyed, and perlitny steel of a zolyama of oxide of aluminum allows to reduce sorption of radionuclides in addition: a) on $^{137}$Cs on the alloyed steel by 6 times, and on perlity steel - by 9 times; b) on $^{60}$Co on the alloyed steel by 6 times, and on perlity steel - by 4 times.

References

[1] Malyshev A B 2007 About the Bulletin on Atomic Energy 8 17-19
[2] Yastrebinskii R N, Bondarenko G G, Pavlenko V I 2016 Radiation resistance of the structural matrix Inorganic Materials: Applied Research 7(5) 718–723
[3] Morozova I K, Gromova A I, Gerasimov V V 1975 Carrying out of products of corrosion of reactor materials (Moscow: Atomizdat) p 190
[4] Antropov L I 1975 Theoretical electrochemistry (Moscow: Himizdat) p 235
[5] Shatalov A Ya 1971 Electrochemical bases of the theory of corrosion of metals (Voronezh: VSU publishing house) p 180
[6] Pettit P, Hesurf J 1980 Decontamination of the Douglas Point Reactor by the Can-Decon Process Materials Perfomance 19(1) p 28
[7] Bracbury D, Segal M 1981 Decontamination of Winfrith SGHWR Cooland Circuits Using LOMJ Reageners Nuclear Energy 20(5) p 56
[8] Zakharova E V, Kazarin V Ch, Meshkova G N 1995 Improvement of methods for decontamination of equipment of the NPP primary circuit Atomic energy 1 71–74
[9] Coch G V, Grurer J 1991 Decontamination during decommissioning Kerntechnik 56(6) 372–375
[10] Venkateswaran G, Kansara H N, Moorthy P N, Wagh P M 1996 Chemical and chemo-mechanical decontamination of the tank system in the clean-up system of TAPS-2 (In ARC Rept – 005) p 29
[11] Bogdanov N I, Nosov A A 1977 Corrosion products in the circuit of the MPTs NPP with
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