Electrochemical decontamination

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ABSTRACT

This paper presents results of electrochemical radiological decontamination of fragments of basic equipment which was used at nuclear power stations and in an experimental nuclear reactor. Equipment made of stainless and low-alloy steels was subjected to radiological decontamination. Mixtures based on orthophosphoric and sulfuric acids were used as solutions for surface treatment. To protect the products being treated against corrosion and to reduce the working current density and electrolyte temperature, inhibiting compositions based on derivatives of aromatic and aliphatic amines and amides were added to the electrolyte. The optimal compositions of reaction mixtures and conditions of electrochemical radiological decontamination, which ensure the polishing regime, have been determined.

Two modes of radiological decontamination of basic equipment have been developed: mode of stationary tanks and mode of external electrodes.

The possibility to conduct electrochemical surface treatment at very small electrode spacing allows one not only to reduce the specific electrolyte consumption but also to greatly reduce the specific electrical energy consumption and to treat the surface of equipment of large geometrical dimensions without dismounting.

It has been shown that it is possible in principle to carry out electrochemical radiological decontamination of articles made of nonconducting materials.

Keywords: electrochemical radiological decontamination, metal surfaces, stationary regime, external electrodes.

INTRODUCTION

The problem of ensuring a high level of safety of the operating personnel of nuclear reactors and reducing the ecological pressure on the environment is an important applied and scientific problem. According to the technological regulations, the equipment of nuclear power stations and experimental reactors (heat-exchange equipment, pipelines and joints, devices for loading fuel elements, etc) is liable to periodical inspection with the object of detecting damages and preventive repair. During operation, this equipment is contaminated by radionuclides, acquires induced radiation and becomes a source of increased danger for the operating personnel and the environment, therefore it requires radiological decontamination.

Besides, as experience shows, emergencies often arise at nuclear power stations. To ensure the safety of the operating personnel and to eliminate the consequences of emergencies, reliable and highly efficient processes and technologies for the radiological decontamination of basic equipment are required.

Under the conditions of nuclear power station, metal surfaces are contaminated mainly by activated corrosion products of structural materials: by the isotopes $^{54}$Mn, $^{55}$Fe, $^{60}$Co, the decay products $^{90}$Sr, $^{137}$Cs, and in the case of fuel-element failure by $^{238}$Pu, $^{239}$Pu, $^{240}$Pu, $^{241}$Am, $^{237}$Np, etc. The radiocontamination of the basic equipment of nuclear power stations and pilot reactor may be arbitrarily divided into in-service contamination and contamination caused by accident. In-service radiocontamination is typical of the equipment of the reactor department and the internal surfaces of the equipment for special water treatment and water purification. Radioactivity caused by accident is most characteristic of reactor, turbine and electrical equipment.

As a rule, the major part of radiocontamination accumulates in metal surface defects (microcracks and microrecesses) of the surface layer, formed by oxide compounds, and can be removed by mechanical, chemical and electrochemical methods [1-3]. The thickness of this layer is estimated to be of the order of 50 µm.

Analysis of the current state of the problem [1-7] shows that among known radiological decontamination methods (chemical, mechanical, electrochemical) only the electrochemical method enables attainment of a high rate of surface layer dissolution and high-quality radiological decontamination at low specific consumption of reagents and electrical energy, ensuring a high corrosion stability of the metal surfaces of the decontaminated equipment.

In spite of the variety of the existing methods for the radiological decontamination of basic equipment, the overwhelming majority of them, including electrochemical methods, call for considerable improvement. For example, it is known that during electrochemical radiological decontamination, the overwhelming majority of metals change into the passive state, owing to which the efficiency of extraction of radionuclides from the surface layer decreases; however, the interrelation between the decontamination conditions (composition of decontaminating solutions and polarization conditions) has not been established. The conditions that allow the transition to stable passivity to be prevented have not been determined.

There is practically no information on the principle of operation of external electrodes, the peculiarities of design approaches to
the supply of decontaminating solutions to the decontamination zone, the use of structural materials. There is no information on the interrelation between polarization conditions, decontaminating solution composition and the dissolution rate of the surface layer of various structural materials, the degree of their decontamination, the specific consumption of electrical power and electrolyte. It is known [5-7] that radioactive isotopes can be extracted from disperse nonconductive materials through electrophoretic phenomena, but there is no information on the radiological decontamination of nonconductive massive materials in an electric field. The lack of this information does not make for wide practical application of highly efficient electrochemical processes.

The prospects of using electrochemical processes for radiological decontamination increases the possibility of using not only direct current, but also alternating current, ultrasonic activation. Using an external electrode, one can decontaminate equipment of large geometrical dimensions without dismounting it from installation site, which cannot be done when using stationary tanks.

The lack of information on the conditions of the electrochemical radiological decontamination of different structural materials under different polarization conditions and in decontaminating solutions of different composition necessitated research in this direction.

The results obtained can be used to work out technological regulations for electrochemical decontamination process.

**EXPERIMENTAL DETAILS**

The dependence of the degree of radiocontamination on electrochemical treatment conditions, the character of radiocontamination and the materials to be decontaminated was determined on the territory of the pilot nuclear reactor of the Institute for Nuclear Research of the Ukrainian National Academy of Sciences. For decontamination, we took fragments of the equipment of the pilot reactor during scheduled preventive repair and specimens from the nuclear power station at Chornobyl.

For electrochemical treatment, current- and voltage-stabilized dc sources were used. The voltammetric investigations were carried out using a Pt-50-1 potentiostat with automatic recording of voltammograms. The voltammograms were recorded in a three-electrode cell with respect to a normal hydrogen reference electrode at a potential scan rate of 2 mV s⁻².

The radiocontamination level of specimens under investigation before and after radiological decontamination was monitored using equipment of the Institute for Nuclear Research of the Ukrainian NAS by means of special devices (KRB-1, RKB4-1eM, MKS-01R radiation meters, gamma-spectroscopic complex).

The mass loss of specimens under investigation during electrochemical treatment was determined by the gravimetric method.

The sight control of the surface condition of specimens under investigation was performed on REMMA-101M scanning electron microscope-microanalyzer.

The change in the mechanical properties of the surface was determined by measuring microhardness.

**RESULTS AND DISCUSSION**

**Voltammetric investigations**

Electrochemical radiological decontamination is based on the dissolution of metal surface layers by the action of both direct current [1-3] and alternating current [8, 9]. The higher the dissolution rate, the higher the decontamination rate. The investigations carried out showed that the overwhelming majority of metals are passivated under anodic polarization by dc. That is conditions exist under which there is practically no dissolution of the surface layer, and hence no decontamination. A typical trend of polarization curve for carbon steel (St.3) in a solution of sulfuric and phosphoric acids is shown in Fig. 1.

![Fig.1. Current-potential curves for carbon steel (St.3) in an acidic decontaminating solution, obtained in the modes: (1) stationary tank at a rate of electrode rotation of 7 rpm; (2) external electrode with rotation; (3) external electrode without rotation. Composition of the solution, wt. %: H₂SO₄, 40; H₃PO₄, 40, H₂O, 20.](image)

The current – potential curve may be arbitrarily divided into three sections. An analysis of the results obtained showed that on the first section (I), dissolution of the surface layer, and hence decontamination, takes place, but the surface of specimens is etched. This decontamination mode is not recommended for articles or equipment of predetermined geometrical dimensions.

There is practically no decontamination at the conditions of anodic polarization, which corresponds to the second section (II, II') of the polarization curve. The metal surface is in the passive state. Treatment of the metal surface, which corresponds to the third section (III, III'), ensures the best decontamination conditions, decontamination being accompanied by polishing in acidic decontaminating solutions based on a phosphoric acid – sulfuric acid mixtures.

The conditions and character of anodic dissolution depend on the nature of metal, the composition of the solution, anodic polarization value. Thus, to optimize the electrochemical radiological decontamination conditions, information on the electrochemical behavior of metals is required.

In the external electrode mode, in contrast to the stationary tank mode, mass exchange between the electrodes is through a porous dielectric material saturated with decontaminating solution. Description of the principle of operation of such a device is given below. The occurrence of electrode processes in the systems where the electrolyte is in the porous material matrix differs from that in ordinary systems, where convective diffusion makes a considerable contribution to mass transfer.

In view of this, current-voltage characteristics for electrodes made of different materials have been investigated under different conditions of mass transfer to the interface. Figure 2 shows schematically electrolytic cells, in which mass transfer to the electrode working surface occurs under the conditions of free (without rotation of the electrode) and forced (with rotation of the electrode, show with an arrow) convection (a) and in a cell where convective transfer is ruled out by a porous dielectric (b).
For the purpose of renewing the electrolyte in the pores of the dielectric material, the surface of the electrode itself was able to rotate.

![Fig. 2. Arrangement of the electrodes in the case of studying the effect of the conditions of solution delivery to the electrode surface on the shape of current-potential curves: (a) stationary tank mode; (b) external electrode mode. Rate of electrode rotation: 7 rpm.](image)

Such variants of disposition of electrodes simulate decontamination in stationary tank and external electrode modes. Carbon steel (St 3), stainless steel (12Kh18N10T) and copper were investigated as materials that were subjected to electrochemical treatment.

The results obtained (Fig. 1) showed that in acidic decontaminating solutions, carbon steel changes to passive state on anodic polarization. The potential of transition to passive state (so-called Flade potential) is 0.0±0.05 V and depends neither on the mode of delivering decontaminating solution to the interface nor on the acid solution composition.

In the stationary tank and external electrode modes in the case of forced solution convection (rate of electrode rotation: 7 rpm), the current density in transition to passive state is about twice higher than without forced solution delivery to the interface.

In the case of forced solution convection in the porous material (translational motion of external electrode relative to the surface being decontaminated), the passivity region decreases in comparison with stationary tank mode, which reduces specific electrical energy consumption.

Moreover, it has been noted that transition from passive state to transpassivation regime in the case of external electrode with its rotation is accompanied by the occurrence of current oscillations. The occurrence of unstable state at the interface contributes to higher rate of the decontamination process.

In comparison with carbon steel, current-potential curves for stainless steel are characterized by a much larger passivity region (0.0 to +(1.4-1.5) V). On current-potential curves there is no clearly defined transpassivation region, therefore it is recommended to carry out radiological decontamination in this case at high current densities. A small shift (of up to 50 mV) towards more positive values on changeover to the external electrode mode with forced solution delivery has been noted.

In comparison with carbon steel, the current densities corresponding to Flade potential are almost half as high. Typical current-potential curves for stainless steel in acidic decontaminating mixtures of different composition are shown in Fig. 3. The numbering of the curves in the figures corresponds to the conditions of solution mass transfer to the interface given in the captions to Fig. 1.

The results obtained give evidence that only external electrode mode gives rise to unstable states (current oscillations) on the stainless steel surface at relatively low potentials (1.5 – 1.6 V) and hence makes dissolution of surface layers possible at low current densities.

Electrochemical decontamination of radioactively contaminated materials

Results of the electrochemical radiological decontamination of different structural materials are given in Table 1. Specimens of the pipeline of the primary coolant circuit (material 12Kh18N10T stainless steel), parts of the heat-exchanger loop: bearing race (40YuT steel), composite: ring with press-fitted bronze bushing (KhN35VTYu steel, BROTs 10-2 bronze), fittings from the reactor room (stainless-clad carbon steel) were decontaminated. Besides, samples of materials removed from the pilot reactor during scheduled repair were decontaminated. These materials were 12Kh18N9T stainless steel, 09G2S steel, beryllium neutron displacer, rubber, polyvinyl chloride, porcelain (Rashek rings), ion-exchange resin.

Metallic specimens were decontaminated in decontaminating solutions of the following composition (wt%): Orthophosphoric acid, 65; Sulfuric acid, 20; Water, 15 and Inhibiting composition (product of polymerization aniline with urotropine and its following condensation), 7.5 vol% with respect to acid mixture.

The nonconducting materials were decontaminated both in an acid solution of the above composition and in a sodium sulfate based solution: Sodium sulfate, 1M; Trilon B, 30 g/L; Seignette salt, 30 g/L.

The basic diagram of the electrolytic cell for the radiological decontamination of nonconducting materials in the field of electrical current is shown in Fig. 4.

![Fig. 3. Current-potential curves for stainless steel (12Kh18N10T) in an acidic decontaminating solution.](image)

![Fig. 4. Basic diagram of an electrolytic cell for the radiological decontamination of nonconducting materials.](image)

The investigation carried out showed that the electrochemical radiological decontamination of surfaces of equipment made of both stainless steel and low-alloy carbon steel ensures a high decontamination level. The exposure rate of radiocountamination of the specimens under investigation after decontamination did not exceed the reference level values allowed for rooms where the personnel work periodically.

The investigations carried out showed that the best effect in electrochemical radiological decontamination is achieved in the...
case of uniform dissolution of the metal surface layer of 20 μm thickness. In some experiments, the rate of the anodic dissolution of the structural materials of which the basic equipment is made was determined (Table 2).

Table 1. Characteristics of radiological decontamination of various materials used in the basic equipment of nuclear reactors

<table>
<thead>
<tr>
<th>Material to be decontaminated</th>
<th>Decontamination conditions, modes of radiological decontamination</th>
<th>Radiocontamination (β decays/cm² min)</th>
<th>Character of radiocountamination</th>
</tr>
</thead>
<tbody>
<tr>
<td>12Kh18N10T stainless steel (a part of the water pipeline of the primary coolant circuit)</td>
<td>Acid solution, i = 35 А/dm², τ = 30 min.; stationary tank</td>
<td>Before decontamination: 5000; After decontamination: 30</td>
<td>137Cs, 134Cs, 60Co, 90Sr</td>
</tr>
<tr>
<td>12Kh18N10T stainless steel (reactor plug)</td>
<td>Acid solution, i = 7 А/dm², τ = 15 min.; stationary tank</td>
<td>Before decontamination: 100; After decontamination: –</td>
<td>137Cs, 90Sr, 60Co, 55Fe</td>
</tr>
<tr>
<td>St3 carbon steel (specimens of fittings)</td>
<td>Acid solution, i = 35 А/dm², τ = 40 min.; external electrode</td>
<td>Before decontamination: 1·10⁶; After decontamination: 3·10³</td>
<td>137Cs, 90Sr, 60Co, 55Fe</td>
</tr>
<tr>
<td>12Kh18N10T stainless steel (inner walls of the “hot” box)</td>
<td>Acid solution, i = 8 А/dm², τ = 3 min.; external electrode</td>
<td>Before decontamination: 200; After decontamination: 10</td>
<td>137Cs, 134Cs, 60Co, 90Sr</td>
</tr>
<tr>
<td>12Kh18N10T stainless steel (equipment for special water treatment)</td>
<td>Acid solution, i = 10 А/dm², τ = 4 min.; external electrode</td>
<td>Before decontamination: 450; After decontamination: 35</td>
<td>137Cs, 134Cs, 60Co, 90Sr</td>
</tr>
<tr>
<td>40YuT steel (bearing race)</td>
<td>Acid solution, i = 20 А/dm², τ = 30 min.; stationary tank</td>
<td>Before decontamination: 5000; After decontamination: 200</td>
<td>137Cs, 134Cs, 60Co, 90Sr</td>
</tr>
<tr>
<td>40Kh steel (spacer sleeves)</td>
<td>Acid solution, i = 5 А/dm², τ = 40 min.; stationary tank</td>
<td>Before decontamination: 2300; After decontamination: –</td>
<td>137Cs, 134Cs, 60Co, 90Sr</td>
</tr>
<tr>
<td>KhN35VT10 steel, BROT's-10-2 bronze (Ring with press-fitted bronze bushing)</td>
<td>Acid solution, i = 15 А/dm², τ = 40 min.; stationary tank</td>
<td>Before decontamination: 8000; After decontamination: 10</td>
<td>137Cs, 134Cs, 60Co, 90Sr</td>
</tr>
<tr>
<td>Beryllium neutron displacer</td>
<td>Acid solution, I = 15А, U = 20 В, τ = 15 хв. stationary tank</td>
<td>Before decontamination: 650; After decontamination: –</td>
<td>137Cs, 60Co, 154Eu, 90Sr</td>
</tr>
<tr>
<td>Rubber seal ring of the primary coolant circuit</td>
<td>Neutral solution, I = 6 А, U = 8 V, τ = 35 min.; stationary tank</td>
<td>Before decontamination: 450; After decontamination: 100</td>
<td>137Cs, 60Co, 154Eu, 90Sr</td>
</tr>
<tr>
<td>Porcelain (Rashek rings)</td>
<td>Neutral solution, I = 6 А, U = 8 V, τ = 35 min.; stationary tank</td>
<td>Before decontamination: 600; After decontamination: 100</td>
<td>137Cs, 134Cs, 60Co, 154Eu</td>
</tr>
<tr>
<td>Porcelain (Rashek rings)</td>
<td>Acid solution solution, I = 15 А, U = 15 V, τ = 35 min.; stationary tank</td>
<td>Before decontamination: 600; After decontamination: 20</td>
<td>137Cs, 134Cs, 60Co, 154Eu</td>
</tr>
<tr>
<td>Polyvinyl chloride</td>
<td>Acid solution solution, I = 15 А, U = 26 В, τ = 30 min.; stationary tank</td>
<td>Before decontamination: 500; After decontamination: 50</td>
<td>137Cs, 134Cs, 60Co</td>
</tr>
</tbody>
</table>

The data are given for an acid solution, whose composition was specified above. The surface layer dissolution rate increases with current density. The largest values are typical of austenitic and carbon steels. Increasing the temperature and the presence of complex additives in acidic decontaminating solutions also make for higher surface layer dissolution rate. For example, whereas in the case of 12Kh18N10T stainless steel the surface layer dissolution rate is 0.6 μm/min at 25 °С and a current density of 15 А/dm², it is 0.8 μm/min at 60 °С.

The change in the mechanical properties of surfaces before and after electrochemical radiological decontamination was studied by X-ray structural and microindenter analysis and optical microscopy. The electrochemical treatment was carried out in an acid solution at a current density of 15 А/dm² for 20 min. Kh18N10T austenitic steel and carbon steel (St3) were investigated. As a result of the research carried out by us, it has been found that after electrochemical radiological decontamination, the number of microdefects, microdislocations
and other microformations of the second kind on the surface decreases (the parameter $\Delta a/a$ decreases). For instance, whereas before treatment the parameter $\Delta a/a$ for St3 was $1.2 \times 10^{-3}$, after treatment it is practically not identifiable. The dislocation density is lower than in the standard. The research carried out by showed that the electrochemical treatment of Kh18N10T austenitic steel and St3 carbon steel makes for their better mechanical properties. The number of microformations and dislocations decreases noticeably, the structurally stressed state improves.

The observed effect may be attributed to the fact that during electrochemical treatment, the surface layer saturated with stress and dislocation concentrators dissolves. On the metal surface is formed, under anodic polarization, a more homogeneous oxide film, which prevents dislocations form reaching the surface and makes for higher plastic resistance.

There are grounds to believe that the improvement of structural and elastic characteristics after anodic electrochemical treatment is determined by the peculiarities of interface processes and formation thereby of a new surface layer.

**External electrode mode**

An electrode design has been developed, in which the porous material can be quickly replaced with the aid of a special mount with rope tie which contact the operating personnel with it. This is especially important in replacing radionuclide-saturated material. The principal scheme of the device is shown in Fig.5. External electrode consists of a telescopic bar 1, on which the handle 2 of a clamping device 5 is fastened, by means of which a porous material 7 is fastened to the operating surface of the electrode 6. By a special tubing 3 decontaminating solution, which is necessary for the electrochemical removal of radionuclides from the surface of the equipment being decontaminated, is conveyed into the porous material 7. Radioisotopes accumulate in this porous material, which is moved over the surface being treated by means of the telescopic bar 1.

![Fig.5. General view of external electrode (its operating part): side view (a) and front view (b)](image)

The following materials are recommended as porous material: polypropylene, silica or basalt multiply cloths. As a result of the investigations carried out it has been found that silica material in the form of multiply cloth shows the highest ability to retain decontaminating solutions. In spite of their higher mechanical stability, polypropylene cloths have a worse ability to retain decontaminating solution. Besides, silica, basalt, carbon cloths and fiber have a much larger sorptive capacity for radionuclides in comparison with polypropylene material. The specific solution consumption in the case of using this material is estimated to be 3-4 g/dm² under the action of direct current. Current is supplied to the operating surface by means of a current lead 4.

In the case of decontamination with direct current, the external electrode acts as a cathode, and the surface being decontaminated acts as an anode.

The working surface area of the electrode is 1 dm², its mass is 2 kg. The maximum current load is 80 A, which enables 80 A/dm² decontamination conditions to be used. The dc power is not over 1.5 kW.

A universal engineering documentation has been worked out, which allows one to organize serial production of external electrodes.

**CONCLUSIONS**

- It has been found that almost all metals whose isotopes contaminate the surface of the basic equipment (light actinides, cesium, strontium, cobalt, iron, nickel, etc) have a more negative ionization potential than stainless and carbon steel, of which the overwhelming majority of basic equipment is made. An exception is nickel, which has a more positive ionization potential (+ 1.65 V) in sulfate solution than stainless steel. This indicates that solutions based on various inorganic acids and their salts can be used for radiological decontamination. The anodic polarization regions in which radiological decontamination is accompanied by polishing have been established.

- Compositions of solutions for the electrochemical radiological decontamination of various structural materials have been proposed. Orthophosphoric and sulfuric acids, sodium sulfate, nitrite and nitrate form the basis of such solutions.

- To reduce corrosion and to improve the decontaminating and polishing ability, complexing agents and inhibiting compositions are added to solutions.

- The conditions ensuring the predetermined decontamination level of various structural materials have been determined, metal loss during decontamination has been estimated.

- The investigations carried out showed that the electrochemical treatment of Kh18N10T austenitic steel and St3 carbon steel makes for their better mechanical properties. The number of microdefects and dislocations is greatly reduced, and the structurally stressed state improves.

- It has been found that not only metallic articles, but also articles made of nonconducting materials are amenable to electrochemical radiological decontamination. A design for the radiological decontamination of nonconducting materials in dc field has been proposed.

- It has been shown that the use of the external electrode mode of electrochemical radiological decontamination makes it possible to greatly reduce the consumption of reagents and electrical energy for radiological decontamination.

- Design documents for making experimental equipment for electrochemical radiological decontamination in two modes: in the stationary tank mode and in the external electrode mode have been worked out.

- Experimental models of external electrodes with an operating surface area of 1 dm² have been made. A design for the fastening of the porous material, which holds the decontaminating solution, to the electrode has been...
developed, which allows one to replace it quickly and conveniently. Designs for the renewal of the decontaminating solution in the external electrode have been found. The designs of external electrodes developed permit one to work with both acidic and neutral salt decontaminating solutions.

− Technological regulations for the radiological decontamination of various materials the stationary tank and external electrode modes have been worked out.

REFERENCES


